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DropBooks

TRACE ELEMENTS BY COPRECIPITATION: EXTRACTION

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In separation by precipitation, contamination with other elements by coprecipitation is undesirable. However, since the publication by Bonner and Kahn of a summary on the separation of carrier-free radioactive tracers by coprecipitation in 1951, this technique has found wider application to the separation and preconcentration of trace elements in various kinds of samples, such as natural water, treated wastewater, high purity metals and geological and biological materials.

In modern textbooks, coprecipitation is recommended for separation and preconcentration of a single trace element or a group of trace elements when the concentration is too low to be directly precipitated or the amount is too small to be handled. In general, coprecipitation of trace elements is carried out with inorganic and organic precipitants attaining high degrees of concentration, so that subsequent determinations can be performed by using the precipitate itself.

Mechanism

Depending on the nature of the solid phase produced in a solution and the experimental conditions, coprecipitation occurs by different mechanisms. Although the various types of coprecipitation cannot be distinguished clearly, they may be classified according to the following mechanisms: (i) the formation of mixed crystals and mixed chemical compounds, (ii) surface adsorption and the occlusion and (iii) mechanical inclusion of trace components into the other compounds during crystal formation. However, these processes often proceed concurrently, making the precipitation process quite complicated.

Isomorphous Mixed-Crystal Formation

The processes of coprecipitation by isomorphous mixed-crystal formation have been well studied, and the distribution of trace elements is found to be governed by either the Berthelot–Nernst or the Doerner–Hoskins law.

Berthelot–Nernst distribution law (homogeneous distribution). If digestion is continued throughout the precipitation process, equilibrium will be established between the trace elements in the interior of the crystals and the solution, resulting in homogeneous distribution of the trace element in the precipitate. Then, the following equation applies:

$$\frac{(\text{Trace element})_{\text{ppt}}}{(\text{Carrier})_{\text{ppt}}} = D\frac{(\text{Trace element})_{\text{soln}}}{(\text{Carrier})_{\text{soln}}}$$

The higher the value of D, the higher the enrichment of trace elements.

Doerner–Hoskins law (logarithmic distribution) When the ions cannot reach the interior of the crystals, equilibrium will be established between the trace elements in the solution and those on an extremely thin surface layer of the crystals. This results in logarithmic distribution of the impurities, and the following equation is applicable:

$$\log\frac{T_{\text{o}}}{T_{\text{s}}} = \lambda\cdot\log\frac{C_{\text{o}}}{C_{\text{s}}}$$

where T and C represent trace element and carrier, subscript o and s denote the concentration in the solution before and after the precipitation, respectively.

In practice, coprecipitation of the trace elements may occur between the above two limiting distribution laws.

Surface Adsorption

The surface of a precipitate is particularly reactive. Ions at the surface of a crystal are incompletely coordinated and hence are free to attract other ions of opposite charge from the solution. The surface adsorption of ions on ionic precipitates has been described by the Paneth–Fajans–Hahn rule which demonstrates that adsorption generally increases with the growing surface area of the crystal and with the decrease in solubility of the compounds of the trace elements which the elements form with oppositely charged ions of the crystal. However, there are many exceptions to this rule. For example, in spite of the low solubility of $PbCl_2$ or PbI_2, they do not coprecipitate with $HgCl_2$ or HgI_2.

Two other factors, the dissociation constant of the adsorbed compounds and the deformation ability of the ions, are important for adsorption. The smaller the dissociation of the adsorbed electrolyte, the larger the adsorptivity. The adsorptivity also increases with increased deformability of the adsorbed electrolyte. The deformability usually increases with the size of the ion.

Another mechanism of adsorption presented by Pauling is an ion exchange process. When the radius of an ion in the solution is similar to an ion on the surface of the crystal, they are exchangeable with each other. This is more effective when an ion in the solution forms slightly soluble compounds with an ion of opposite charge in the crystals. Thus, lead (II) ions can be adsorbed on the surface of a barium sulfate precipitate even in the absence of excess sulfate ion in the solution, according to the following exchange reactions:

$$BaSO_4(\text{surface}) + Pb^{2+} \rightarrow PbSO_4(\text{surface}) + Ba^{2+}$$

Occlusion and Mechanical Inclusion

When an ion adsorbed on a crystal surface from the solution is trapped by subsequent crystal layers, the ion will be occluded in the interior of the precipitate. This situation can be prevented with colloidal precipitates rather than with crystal ones, especially in a rapid precipitation process. For example, freshly precipitated hydroxides or sulfides contain a certain amount of impurities, most of which are released upon ageing of the precipitates. Thus, coprecipitation by occlusion generally gives a poorly reporducible yield of the trace elements to be coprecipitated.

Coprecipitation with Inorganic Precipitants

Coprecipitation of trace elements with inorganic precipitants is usually carried out using colloidal precipitates with a large surface area such as metal hydroxides and sulfides. Among various hydrated oxides, coprecipitation with those of iron(III) and manganese(IV) have been commonly used and are the most studied, but many other hydroxides, such as $Al(OH)_3$, $Be(OH)_2$, $La(OH)_3$, $Th(OH)_4$ and $Zr(OH)_4$, and mixtures of metal hydroxides, such as $Fe(OH)_3$ and $Ti(OH)_4$, have also been employed.

Coprecipitation techniques are commonly used to separate and concentrate trace elements from very dilute solutions, such as natural water. Since the solubilities of the metal hydroxides or sulfides are mainly governed by the pH value of the solution,

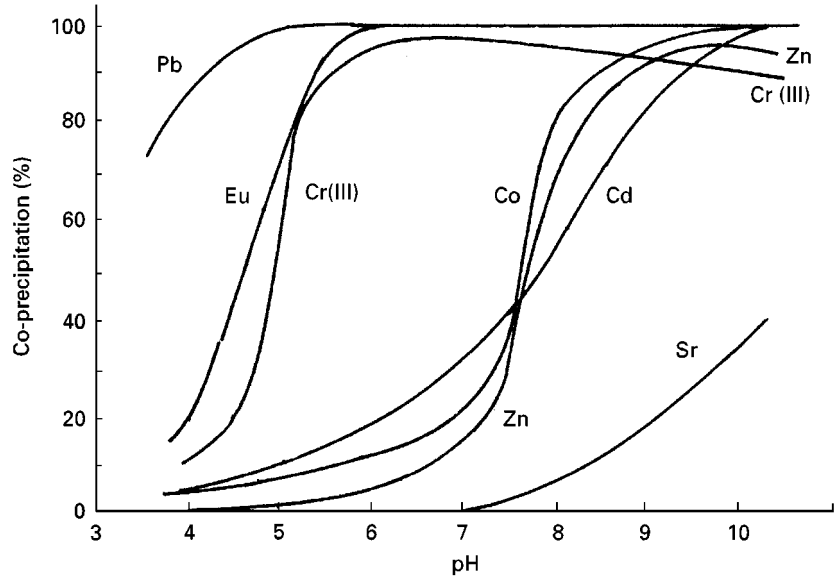

Figure 1 Relation between co-precipitation recoveries of metals with iron(III) hydroxide and pH of the solution.

control of pH is essential for an effective coprecipitation of trace metals. **Figure 1** shows coprecipitation yields of some metal ions with iron(III) hydroxide. It can be seen that removal of many metal ions from a solution may be possible at pH 9–10. However, it should be noted that the coprecipitation yield is also affected by the amounts of precipitants used, the coexisting salts and the ageing time of precipitation. Since most metals form sparingly soluble hydroxides, coprecipitation by hydrated metal oxides is usually of low selectivity, so that different trace metals are likely to be coprecipitated simultaneously.

Three possible mechanisms relating to the adsorption of the trace metal ion on the hydrated metal oxide surface prior to coprecipitation have been suggested.

The first involves ion exchange between adsorbed hydrogen on the hydrated oxide surface and the trace metal ion M in solution according to the equation:

$$n\overline{SH} + M^{m+} \overset{k_n}{\rightleftharpoons} \overline{S_nM}^{(m-n)+} + nH^+$$

where n is the number of molecules of the hydrated metal oxide and the surface area per molecule is S. M represents the metal cation of charge m. Then the distribution coefficient D is given by:

$$D = \frac{[M]_{surface}\,(\text{mol kg}^{-1})}{[M]_{solution}\,(\text{mol dm}^{-3})} = \frac{K_n\overline{SH^n}}{(H^+)^n}$$

By taking logarithms the equation becomes:

$$\log_{10}D = n\text{pH} + \log_{10}(K_n) + n\log_{10}(SH).$$

The second postulated mechanism involves the chemical sorption of the trace metal ion M^{m+} on the surface of the hydrated metal oxide, followed by the adsorption of hydroxyl ions:

$$\overline{S} + M^{m+} = SM^{m+}$$

$$SM^{m+} + OH^- = SMOH^{(m-1)+}$$

$$SMOH^{(m-1)+} + OH^- = SM(OH)_2^{(m-2)+}$$

The third possible mechanism requires the adsorption of hydrolytic complexes of the trace metal ion, rather than the metal ion itself, on the surface of the hydrated metal oxide:

$$M^{m+} + nH_2O = M(OH)_n^{(m-n)+} + nH^+$$

$$\overline{S} + M(OH)_n^{(m-n)+} = SM(OH)_n^{(m-n)+}$$

Table 1 shows examples of preconcentration of trace elements by coprecipitation with inorganic precipitants.

Coprecipitation with Organic Collectors

Organic collectors are mainly complexing agents which are sparingly soluble in aqueous solution and form complex compounds with the desired metal ions. The mechanisms of coprecipitation of trace elements with organic collectors have been described by Minczewski *et al.* According to them:

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Table 1 Coprecipitation of trace elements with inorganic precipitants

Precipitants	*Trace elements*	*Sample, experimental conditions, comments*
Hydroxides		
Al(III)	Cr(III), (VI), Mo, W	Natural waters. Quantitative precipitation: Cr(III) (pH 5–9), Mo (pH 4–5), W (pH 6–8), Cr (VI) (pH 5–6, but it is not quantitative)
	Ce, Eu, La, Lu, Nd, Sm, Tb, Th, Tm, Yb, U	Hot spring and crater waters. 10 mg Al to 2 dm^3 sample. Al precipitation is carried out at near boiling temperature with 14% NH_3 solution to reach pH 6.5–7.5
	Th, U	Hot spring and crater lake waters. $Al_2(SO_4)_3$ (25 mg) is added to 1 dm^3 sample. pH is adjusted to 7–8 with 14% NH_3 solution
	Li	Geothermal waters: pH should be high ($>$12.5–13) and a long mixing time is required. The recovery yield is increased by removal of Ca ions and polymerized silica
Be(II)	As	High purity iron steel. Sample (1 g) is digested with HNO_3. 5 cm^3 $BeSO_4$ (1 mg Be/cm^3) is added in the presence of EDTA (mask matrix elements). As coprecipitates as $BeNH_4AsO_4$ with $Be(OH)_2$. Perfect recovery is obtained between 1.0 and 3.5 mol L^{-1} HCl with relative standard deviation (RSD) of *c.* 13% for 1.0 μg g^{-1} As. Detection limit is 0.3 μg g^{-1} of solid sample
	P	High purity iron steel. Same procedure as As. Coprecipitation recovery is 98.7%. Arsenic is removed from the solution as $AsBr_3$ for Mo-blue spectrophotometry of P
Bi(III) + In(III)	Co, Cu, Fe, Mg, Ni	High purity Ti metal. 0.5 g sample is dissolved in 6 mol L^{-1} HCl (20 cm^3) + HF (0.5 cm^3). Bi(III) and In(III) are added (10 mg and 20 mg, respectively). After addition of 4 cm^3 of H_2O_2, pH is adjusted to 9.5 with 7.5 mol L^{-1} NaOH (pH $>$ 11 for Mg). Ageing time 30–60 min. Perfect recoveries are obtained for all metals. RSD: 0.22%. 0.28%, 2.8%, 0.05% and 0.84%. Detection limit: 0.10, 0.5, 1.8, 0.08, 0.36 μg g^{-1} for Co, Cu, Fe, Mg, Ni, respectively
Fe(III)	Cd, Co, Eu	Seawater. Coprecipitation yield in the radionuclide levels: Cd (85% at pH 9.0, Fe 35 mg dm^{-3}), Co (95% at pH 9.0, Fe 35 mg dm^{-3}), Eu (*c.* 100% at pH 9.0 Fe 10 mg dm^{-3}, at pH 6.0–9.0, Fe 35 mg dm^{-3})
	Mo	Seawater. To 500 cm^3 sample, 9 mol L^{-1} H_2SO_4 (1.0 cm^3) and 0.1 mol L^{-1} $FeCl_3$ (3.0 cm^3) are added. *c.* 96.5% coprecipitation yield of Mo is obtained at pH 4.0; it decreases with increasing pH value
	Cr(III), (VI)	Urine. Cr(III) is found to be precipitated at pH 10, while Cr(VI) remains in the solution. Cr(VI) is only coprecipitated at 4–7
	Cr(III)	Seawater. 4 cm^3 of 2 mol L^{-1} HCl, 4 mg Fe(III) are added to 2 dm^3 sample, heat to 50–60°C, 60 cm^3 borate buffer (19.07 g borate + 4 g NaOH in 1 dm^3) is added to solution to pH *c.* 7.5. Recovery for Cr $>$ 99% at concentration 0.4 μg dm^{-3}. Precision is $\pm$ 0.02 μg dm^{-3}
	As, Cr, Ge, P, Sb, Se, Te, W	Water sample. Optimum pH ranges are 5–7 for Sb and Se, 5–8 for As and W, 5–10 for Cr, Ge and Te, 6–7 for P. Preconcentration factor is 50 for all except Se, where it is only 5
	Cu, Mn, Ni, Pb, Zn	Natural waters. 2 mg Fe(III) is added to 200 cm^3 sample; pH adjusted to 9 (NaOH). Detection limit is *c.* 1 μg dm^{-3}. ICP-AES is employed
	Se	Seawater, silicates, marine organisms. 20 mg Fe(III) is added to 5 dm^3 seawater, pH is adjusted to 5–6. After 2 h standing, another 20 mg Fe(III) is added to solution, pH to 4–6 with aq. NH_3. RSD is 6.0% for 0.5 μg Se dm^{-3}
	V	Seawater, natural water, biological materials, sediments, rocks. 15 cm^3 1.0 mol L^{-1} HCl and 30 mg Fe(III) are added to 3 dm^3 seawater; pH is adjusted to 5–6 with aq. NH_3. Precipitate is dissolved in 10–20 cm^3 2 mol L^{-1} HCl. Coefficients of variation are 2.8% for seawater, 1.3% for silicate rocks, 2.5% for marine plants. Quantitative recovery is attained for 1.8 μg V dm^{-3}
	Ag, Cd, Ce, Cr, Cs, Er, Eu, Gd, La, Mn, Rb, Sr, Yb	Low level waste solution. Effect of pH was studied. Sorption of Cs^+ and Rb^+ is not strongly pH-dependent, but coprecipitation is low (20%)
	Zn	Quantitative recoveries are obtained for Ag (pH $>$ 8), Cd, Mn, Zn (pH $\sim$ 10), Cr(III) (pH 9–10), Ce, Er, Eu, Gd, La, Yb (pH $\sim$ 10). Sr (pH 11–11.5, 65%). Freshly precipitated $Fe(OH)_3$ can be used for the decontamination of radionuclides
	Te	Hair. Sample (2–4 g) is digested with a mixture of HCl + $HClO_4$, heated to evolving fumes, then boiled with 20% HCl to reduce Te to Te(IV). 5 mg Fe(III) is added, pH is adjusted to 9, and centrifuged. Precipitate is dissolved with 3.3 cm^3 conc. HCl, then diluted to 10 cm^3. Recovery is 96.2 $\pm$ 2.4% for 0.2 μg Te

(Continued)

Table 1 *Continued*

Precipitants	*Trace elements*	*Sample, experimental conditions, comments*
Hydroxides		
Ga(III)	Al, As, Cd, Co, Cr, Cu, Fe, La, Mn, Ni, Pb, Ti, Y, Zn	Seawater. 5 mg Ga is slowly added to 1 dm^3 seawater. pH is adjusted to 9.0 (NaOH), ageing for 24 h. Precipitate is washed with H_2O (remove Na, Mg, K, Ca), dissolved with 2.5 cm^3 1 mol L^{-1} HCl, diluted to 5 cm^3. 200-fold concentration is achieved. Quantitative recoveries are attained at pH 9.0 for Al, Co, Cr, Cu, Fe, La, Mn, Ni, Ti, Y, Zn. As(III), Cd, Pb (<90%, pH 10)
In(III)	Cu, Fe, Ni	Ti alloy. Sample (0.2 g) is dissolved in HCl, 3 cm^3 H_2O_2 is added to mask Ti. 10 mg In(III) is added, pH is adjusted to 9.0 (NaOH). 100% recoveries at pH 8.5–9.0. Detection limit: Cu 0.8, Fe 8.1, Ni 1.4 μg g^{-1} alloy
	Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb	Natural waters. 10 mg In(III) to 100 cm^3 sample. pH to 9.5. Precipitate is separated by centrifuge, dissolved in 1 cm^3 2.5 mol L^{-1} HBr. All are quantitatively coprecipitated. Determination limits for GF-AAS are Cd 0.003, Cu 0.02 μg dm^{-3}
La(III)	As, Bi, Sb, Se, Te	Mo metal. 1 g Mo is dissolved in a mixture of 2 cm^3 conc. HNO_3 + 6 cm^3 conc. HCl. 50 mg La and small amount filter paper pulp to solution. pH is adjusted to 10.0 (NaOH). After filtration, precipitate is dissolved four times with 2 cm^3, boiling 6 mol L^{-1} HCl. Coprecipitation and dissolution are repeated. Recoveries at pH 10.0, As 96.8, Bi 112.0, Sb 92.4, Se 100.1, Te 106.0% for each 5 μg
	Co, Fe, Mn, Ni, Zn	Seawater. 5 mg La to 1 dm^3 sample, pH adjusted to 9.8 with 1 mol L^{-1} Na_2CO_3. Precipitation at 80°C for 30 min and later aged for several hours
Mn(IV)	Bi, Pb, Sb, Sn	Ni matrix. Ni is dissolved with 25 cm^3 (1 + 1) HNO_3, pH adjusted to 2–3 with (1 + 1) aq. NH_3. Volume is made up to 200 cm^3 by adding 0.008 mol L^{-1} HNO_3. MnO_2 is formed from $MnSO_4$ + $KMnO_4$ in the presence of acids with 2-min boiling followed by standing for 30 min. Precipitate is treated with 50 cm^3 10 mol L^{-1} HCl. 100% coprecipitation for Bi, Sb, Sn in 6.5 mg Mn precipitated, while Pb in 30 mg Mn, each in 1–100 μg dm^{-3}
	Mo	Seawater, silicates, biological materials. 1.0 dm^3 water is pH adjusted to 2 with dil. HCl. Each 2 cm^3 ethanol and 1 mol L^{-1} $KMnO_4$ is added and stands overnight. Precipitate is dissolved in saturated aqueous solution of SO_2. Quantitative coprecipitation is in the range of pH 1.3–5.5 for Mo level < 5 μg dm^{-3} seawater
	Ga	Aqueous solution. Coprecipitation conditions are studied. To 200 cm^3 solutions containing Ga (0.5–1000 μg) 5 cm^3 5% $MnSO_4$ is added and adjusted pH to 1.5–1.6 with HCl or H_2SO_4, to boiling and slowly added 2.5 cm^3 1.25 mol L^{-1} $KMnO_4$, then stands for 5–7 min. Precipitate is dissolved in 10 cm^3 5% HCl containing 8–10 drops 3% H_2O_2. Ga is perfectly recovered
	As	Cu, Fe, Ni metals. Sample (0.1–2.0 g) is dissolved in 20–30 cm^3 HNO_3(1 + 1). pH to 1.0–2.0 with aq. NH_3 (except for Fe). As is coprecipitated by adding 60 mg $KMnO_4$ + 10 mg Mn(II). Precipitate is dissoved in mixture (HNO_3 + H_2O_2). Detection limit: 20 ng cm^{-3}
Te(IV)	Se	High salt waste water. After boiling 100 cm^3 of sample (1 mol L^{-1} HCl) for 30 min in the presence of 5 g hydrazinium sulfate p.p.b. level Se(IV,VI) is quantitatively coprecipitated with 25–500 μg Te(IV) and completely collected on nitrocellulose membrane filter (pore size 0.2 μm). Heavy metals (high level) do not interfere
	Ag, Au, Pd, Pt, Rh	Cu, Fe, Ni-ores. 1 g sample is dissolved with aqua regia (10 cm^3) at 180°C for 5 h and diluted to 100 cm^3. 10 cm^3 is evaporated, leached with 0.5 mol L^{-1} HCl, Ag is trapped on Dowex 50 w × 8 column and eluted with 0.5 mol L^{-1} HCl. Au, Pd, Pt, Rh in 2 mol L^{-1} HCl are coprecipitated by adding 5 mg Te ($TeCl_3$) and $SnCl_2$ (28%)
Th(IV)	Mo	Seawater. To 500 cm^3 seawater (1 cm^3 9 mol L^{-1} H_2SO_4) is added 3–4 cm^3 0.1 mol L^{-1} $Th(NO_3)_3$, adjusting pH to 6.0 (aq. NH_3) and standing for 30 min. Precipitate is collected on millipore filter, dissolved in HCl. Precipitation yields: 99.5 (pH 6.0), 81.5 (pH 7.5), 61.6 (pH 8.5)
Zr(IV)	Bi	Sea-, spring-, river waters. To sample $ZrOCl_2$ is added, pH to 9.0 with aq. NH_3. Precipitate is dissolved in 4 mol L^{-1} HCl. Quantitative recovery is obtained at Zr > 10 mg in the pH range 8.8–9.2. > 0.5 mg Al, As(III), Cu, Sn interfere
	Cd, Cu, In, Pb	Sediments. To sample solution containing 0.04 g sediment, 1 cm^3 $ZrOCl_2$ is added and pH is adjusted to 8.8. Precipitate is dissolved in 25 cm^3 4 mol L^{-1} HCl. 0.01 μg g^{-1} In in sample solution is quantitatively recovered with > 5 mg Zr at pH 8.4–8.8. Cu and Pb are quantitatively collected at pH 8.25–9.0. 0.05 mg As, Bi interfere with Cu determination; 0.05 mg Sn(II), 0.1 mg As(III), Tl(I) interfere with Pb determination. Optimum pH for Cd is 9.0

(Continued)

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Table 1 *Continued*

Precipitants	*Trace elements*	*Sample, experimental conditions, comments*
Hydroxides		
	Sb	Seawater, algae, silicates. 1 dm^3 water is added 3 cm^3 6 mol L^{-1} HCl and 300–400 mg $K_2Cr_2O_7$, heating to 75–85°C for 1 h. After cooling, 150 mg $ZrCl_4$ completes dissolution; pH is adjusted to 5.0 ± 0.3, ageing at least 90 min. Recoveries of Sb 99.2% (pH 3.0), 99.1% (pH 5.0), 93.7% (pH 7.5). Standard deviation: 0.003–0.009 μg dm^{-3} for 0.08–0.42 μg dm^{-3} Sb
Sulfides		
Bi(III)	As, Sb, Se	Water samples. Coprecipitation is carried out in 1.2 mol L^{-1} HCl solution. Minimum amounts: As(III) 10 ng, Sb(III) 50 ng, Se 20 ng
Cd(II)	Cr, Cu, Fe, Mn, Pb, V	$BaCl_2$ solution. Coprecipitation conditions are studied for 1 μg of Cr, Fe, Mn, Pb, V, 0.1 μg of Cu. CdS is precipitated from $Cd(CH_3COO)_2$ with Na_2S. Optimum conditions: pH 7–8, $BaCl_2$ 15%
In(III)	Co, Cr, Cu, Mn, Zn	Calcite. 0.3 g sample is dissolved with HF, HNO_3 and $HClO_4$, diluted to 200 cm^3. 30 mg In is added; pH adjusted to 9.0. In_2S_3 is precipitated by adding 0.1 g thioacetamide. Coprecipitation recoveries: Co 89.4%, Cr 94.5%. Cu 88.8%, Mn 94.9%, Zn 89.1% for each concentration of 25 p.p.m.
Pb(II)	Cu	Tap water, iron and steel. 30 cm^3 tap water is acidified with 0.5 cm^3 6 mol L^{-1} HCl. After adding 1.0 mg Pb, PbS precipitates by passing H_2S. Precipitate is dissolved in conc. HCl (1 cm^3). RSD: 0.7% for 5 μg dm^{-3}
Sulfates, **phosphates**		
Pb(II)	Cr(III)(VI)	Seawater. Na_2SO_4 (0.2 mol L^{-1} 8 cm^3) added to 800 cm^3 sample; pH adjusted to 3; 8 cm^3 $Pb(NO_3)_2$ added dropwise. Precipitate filtered on Nuclepore. Cr(VI) only coprecipitates with $PbSO_4$ at pH 3. To another 800 cm^3 sample 3 cm^3 0.2 mol L^{-1} $Pb(NO_3)_2$ and 0.2 cm^3 1 mol L^{-1} $NH_4H_2PO_4$, pH adjusted to > 6 with aq. NH_3. Both Cr(III), Cr(VI) are quantitatively coprecipitated with $Pb_3(PO_4)_2$. In seawater, molar ratio of Pb to PO_4^{3-} is kept at 3 for perfect recovery of Cr (VI). 0.08 μg dm^{-3} Cr is detectable
Bi(III)	Am, Cm, Np, Pu	Sequential separation by coprecipitation with $BiPO_4$, by using suitable oxidizing and reducing agents. Cm(III) is separated from Am, Np, Pu, U in their (VI) valency states by adding $K_2S_2O_8$-Ag^+ before coprecipitation. Next, Am(III) is separated from Np, Pu, U by adding C_2H_5OH. Pu(IV) is separated from Np and U by adding $NaNO_2$. Last, Np(IV) is coprecipitated by addition of H_2O_2. Recoveries: Cm (98.5%), Am (97.6%), Pu (94.7%) and Np (96.0%)
Fluorides		
Ca(II)	Cu, Fe	Surface adsorption was shown to be the main cause for coprecipitation. Cu(II) is coprecipitated as counter ion to excess F^-, whereas Fe(III) coprecipitates as FeF_6^{3-} in competition with matrix fluoride
	U	Aqueous solution. To sample 5 cm^3 1 mol L^{-1} $Ca(NO_3)_2$, 30 cm^3 0.3 mol L^{-1} NH_4F solutions are added dropwise. Applicable to coprecipitation of 0.01 ng dm^{-3} U
	Th	Uranium ore. 1 g sample is digested in 50 cm^3 of mixture (8 mol L^{-1} HCl + 0.01 mol L^{-1} $(NH_4)_2SiF_6$) by heating for 4 h. To solution 10 mg La carrier, HF is added to precipitate LaF_3. Precipitate is dissolved with 16 mol L^{-1} HNO_3. Recovery of ^{234}Th tracer is 85% with RSD of $\pm$ 12% for 1 p.p.m. level
Oxalates		
Ca(II)	La, Lu, Tb	Biological materials. Substoichiometric precipitation of rare earth elements was studied. To 8 cm^3 of solution containing 0.0125 mol L^{-1} Ca(II), 2.0×10^{-7}–6.0×10^{-5} mol L^{-1} radioactive RE(III) and 1.25×10^{-3} mol L^{-1} CCl_3COOH – 0.1 mol L^{-1} oxalic acid. At pH 2–5 complete coprecipitation is attained
	Ce, Pm, Sr, Y	Urine. 500 cm^3 is wet-ashed. Resulting salt is treated with 30% H_2O_2, dissolved in H_2O, pH is adjusted to 3.0 (aq. NH_3). Oxalate is removed by dissolving precipitate in hot HNO_3, heating in the presence of 70% $HClO_4$. Residue is treated with H_2O_2 to reduce Ce(IV) to Ce(III) followed by dissolution with H_2O. Recoveries: Ce 87%, Pm 89%, Sr 100%, Y 64%

(Continued)

Table 1 *Continued*

Precipitants	*Trace elements*	*Sample, experimental conditions, comments*
Salts and metals		
AgCN	Pd	Pure metals. Highly selective for Pd in 10^7–10^9 fold excess of Ag, Al, Bi, Cd, Co, Cu, Fe, Mn, Ni, Pb, Sn, Th, Tl, U, Zn. Coprecipitation of Pd is not influenced. Pd is coprecipitated with AgCN. RSD 4–16%; detection limit: 10^{-7}% Pd
As	Se, Te	Geological and biological samples. After digestion of samples by mineral acids ($HNO_3 + HClO_4$). Na_3AsO_3 (*c.* 1.5 mg As) is added. As(III) is reduced to elemental As by phosphorous acid at 80°C for 15 min. Ageing at room temperature for at least 8 h to complete flocculation. Detection limit is 0.1 p.p.m. of Se and Te

1. The sparingly soluble organic compound, such as a bulky organic cation, forms an ion pair with the anionic complex.
2. An insoluble salt formed between the organic anion and the metal cation is coprecipitated together with the excess of the reagent, e.g. metal-8-quinolinate in excess of 8-hydroxyquinoline.
3. A soluble chelate compound of a trace metal can be coprecipitated with the precipitate formed between the excess of the reagent and a bulky different organic reagent cation.
4. An inner complex of the metal ion to be separated is coprecipitated with a large excess of the organic reagent such as 1-(2-pyridylazo)-2-naphthol.

Table 2 Coprecipitation of trace elements with organic collectors

Collectors	*Trace elements*	*Samples, experimental conditions, comments*
Organic carriers		
α-Benzildioxime (α-BD)	Ni	Seawater. 500 cm^3 samples, 1 mg α-BD, pH ~9.5. Ageing time can be minimal. Even 0.2 p.p.b. Ni can be determined
DDTCA (diethyldithiocarbamic acid)	As, Cd, Cu, Fe, Mn, Ni, Pb, Se, Zn	Water samples. Ni, Cu are completely precipitated between pH 1 and 11. Cd, Fe(III), Pb, Zn begin to precipitate at pH 1–2 but complete precipitation is only obtained above pH 4 (pH 5 was used). Complete recovery of As is only obtained at pH 5.0–5.5. For very pure water, metal carrier should be used. Citrate is a powerful masking agent for Fe
	Co, Eu, Mn, Zn	Natural water samples. To 250 cm^3 sample, 20 cm^3 2% (w/v) NaDDTC solution and 5 cm^3 buffer solution (pH 5) are added. Coprecipitation capacity: 900 μmol L^{-1}. Recoveries: Co 97–98%, Eu 88–100%, Mn 85–98%, Zn 82–100%
	Cu, Fe, Hg, Zn	Saline water. To 250 cm^3 sample, 400 mg freshly prepared NaDDTC is added at pH 4.0
DDTCA + dibenzylidene-D-sorbitol (DBS)	As, Cd, Cr, Cu, Fe, Mn, Pb, Sb, Zn	Industrial wastewater, river water. Concentration range 1–50 μg. pH 5.0–5.5 (acetate buffer). 100 mg NaDDTC, 17 mg DBS as flocculant. 94–100% recovery for Mn
Diethylammonium *N,N′*-DDTC	Cd, Cr, Cu, Hg, Ni, Pb	Drinking, wastewaters. To 500 cm^3 sample is adjusted pH to 5.0–5.5 (acetate buffer), then diethylammonium *N,N′*-DDTC is added to make 2%. Recovery ranges: Cd 84–94%, Cr 86–102%, Cu 94–106%, Hg 100–108%, Ni 99–110%, Pb 88–92%
DBDTCA (dibenzyldithiocarbamic acid)	As(III),(V), Cd, Fe, Zn	Fresh water. pH 2. 100 cm^3 samples, 10 mg of Na-salt of DBDTCA in methanol added. As(III) coprecipitates but not As(V) which precipitates after reduction to As(III) with KI + $Na_2S_2O_3$. Recovery of As(III) 100% in pH range 1–3 but drops drastically for higher pH. 2–3 mg of DBDTCA is sufficient. High recoveries are obtained for Cd, Fe and quite high (87.5%) for Zn
DBDTCA + phenolphthalein	Se(IV)	Fresh water and seawater. 500 cm^3 sample is adjusted to pH 2. 10 mg of Na-salt of DBDTCA and 100 mg phenolphthalein in methanol are added. Without phenolphthalein, recovery is 97% but decreases with ageing time. pH should be < 4. In the presence of phenolphthalein ageing does not reduce the yield
Dithizone	Ag, Bi, Cd, Cu, Hg, Pb, Pd, Zn	Dilute HCl and HNO_3 solutions. After adjusting acid concentration, 0.1 g ascorbic acid added to reduce Fe(III), finally dithizone is added. Recoveries depend on the acid concentration. (HCl, M, recovery, %) Bi ($10^{-2} - 5 \times 10^{-2}$, 95), Cd (<0.002, 95), Cu (<2, 95), Hg (<1.5, 95), Pb (<0.001, 95), Pd (< 1, 95), Zn (3×10^{-4}, ~40)

(Continued)

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Table 2 *Continued*

Collectors	*Trace elements*	*Samples, experimental conditions, comments*
Dithizone + phenolphthalein	Ag, Co	Surface water. 4 dm^3 water to be made 0.5 mol L^{-1} H_2SO_4 solution; About 28 mg dithizone and 300 mg phenolphthalein are added. Phenolphthalein helps in collecting the precipitate. At pH 1 only Ag is coprecipitated. Co is recovered quantitatively at pH 6.5–8. Dithizone in glacial CH_3COOH, phenolphthalein in ethyl alcohol
2-Mercaptobenzimidazole (MBI)	Ag, Au, Hg, Sn, Ta	Seawater. Recoveries were studied at pH 1, 3, 5. To 20 dm^3 seawater (pH 1) 5 g MBI in 100 cm^3 ethanol were added and aged for 2 days (0–5°C). High recoveries are obtained at the following pH ranges: Ag (1–5), Au(1), Hg(1–5) Sn(5), Ta(1–3)
Nioxime (1,2-cyclohexanediondioxime)	Ni	Aqueous solution. Selective precipitation of Ni at μg level at pH 7.0–9.5. Large amounts of Co, Cu, Fe are masked with Na-tartrate and Ca-EDTA. 32 mg nioxime is used
Oxine (8-hydroxyquinolinol)	Ce, Fe, Pr, Pu	Aqueous solution. Fe was co-crystallized with oxine produced *in situ* by hydrolysis of 8-acetoxyquinoline. Ce, Pr, Pu also quantitatively recovered
	Cd, Cu, Mn, Pb, Zn	Seawater. The metal ions are quantitatively precipitated in pH range 7.0–8.5 with oxine alone (5 cm^3 of 2% solution) kept at 70°C for 3 h. Detection limits (ng dm^{-3}): Cd 1.4, Cu 10, Mn 5, Pb 10, Zn 6. Recoveries > 98%
	Al	Aqueous solutions. 100 cm^3 sample, pH 6.8–6.9 (0.07 mol L^{-1} phosphate buffer). Slow addition of 160 mg oxine. Ageing 1 h. Sensitivity 0.1–0.02 p.p.m.
PAN (1-(2-pyridylazo)--2-naphthol))	Cr(III), Cu, Hg, Mn, Ni, Zn	Seawater. 0.5–4 dm^3, metal ions are precipitated by adding 20 mg of PAN ethanol solution and heating at 70–80°C for 10 min at pH 6.5–10 for Cu, Ni, Zn; high pH ~ 10 for Cr(III), Mn. It is preferred that pH should be ~9 in order to decrease coprecipitation of Ca. Alkali and alkaline earth metal ions do not interfere
Organic carriers		
	U	Seawater, tap water, digestate of biological samples. Coprecipitation is most effective at pH 4.5–6.5 with recovery of 85–94%. In the presence of 1,2-cyclohexylenedinitrilo tetra acetic acid (CyDTA) as a masking agent. The method is highly selective for U. Detection limit: 3–4 ng dm^{-3} for 500 cm^3 samples and 5 μg kg^{-1} for 0.5 g biological samples
Thionalide (2-mercapto-*N*-2-naphthylacetamide) + Oxine	AS(III), Cu, Sb(III)(V)	Seawater. 0.005–0.25 mol L^{-1} H_2SO_4. As is only precipitated quantitatively at H_2SO_4 > 0.2 mol L^{-1} As(V) is reduced to As(III) by ascorbic acid. 0.015 mol L^{-1} H_2SO_4 is used for total As precipitation. 8 cm^3 2% thionalide in acetone is used. Sb and Cu are coprecipitated with oxine at pH 6–9 while As is not coprecipitated at all
TPAC (tetraphenylarsonium chloride)	$^{96}TcO_4^-$	Aqueous perchlorate solution. Recovery is constant at pH in the range 0.5–13. Precipitation yield is highly affected by TPAC and ClO_4^- concentrations. At 25°C, > 90% yields are obtained at TPAC > 0.02 mol L^{-1}. Coprecipitation of Tc(IV) is very low
Metal + organic carriers		
Fe $(DBDTC)_3$	U	Natural waters. To 500 cm^3 sample. 20 μg Fe(III) and 2 cm^3 0.1 mol L^{-1} KH_2PO_4(pH 4) are added prior to pH adjustment to 4.0 ± 0.02. DBDTC (1%, 1 cm^3) is added, stirring (15 min), ageing (15 min). Detection limit is 0.4 p.p.b.
Fe $(TMDTC)_3$ (tetramethylenedithiocarbamate)	Cd, Co, Cu, Ni, Pb	Mineral water. 0.5 mg Fe(III) to 200–250 cm^3 sample, pH to 2–3, CO_2 is boiled out, 50 mg TMDTC is added. The choice of Fe(III) is due to its high concentration in mineral water. High recoveries are obtained > 95%
$Co(PDC)_3$ (pyrolidine dithiocarbamate)	Cd, Cu, Ni	Seawater. 100 cm^3 samples are adjusted to pH 2 (6 mol L^{-1} HCl). 50 μg Co (as $CoCl_2$), 10 mg APDC are added and aged for 5 min. Precipitate is dissolved in acetone
$Pb(PDC)_2$	Co, Cu, Hg	Dead Sea surface water. To 1 dm^3 sample 2.5 mg Pb is added, pH to 3.6, and 20 mg APDC is added. Determination by X-ray fluorescence
Al-oxinate or In-oxinate	Co, Cu, Mo	Agricultural sample digestate. Al-oxinate perfectly recovers Co, Mo, but not Cu. Addition of thionalide or tannic acid or both leads to quantitative recovery for both Al- and In-oxinates. To a 500 cm^3 sample 15 mg Al, 500 mg oxine are added; pH to 4.5; 200 mg tannic acid, 20 mg thionalide
Mg-oxinate	Al, Cd, Co, Cu, Mn, Ni, Pb, Zn	Aqueous solutions. To 100 cm^3 solution, 20 mg Mg^{2+}, 100–200 mg oxine are added at pH 9.
	Cr(III), Mo, V	Ageing at 70°C for 1 h. Recoveries: 100% except for Cr (83%), Mo (64%), V (70%). Cr recovered at 98% at pH 10.5

5. A chelate of the trace metal is adsorbed and coprecipitated with a water-insoluble organic compound. Several metal dithizonates can be coprecipitated with phenolphthalein.
6. The metal ions are coprecipitated by means of colloidal–chemical sorption on a mixture of insoluble organic reagents.

Typical examples of the coprecipitation of trace metals with organic collectors are listed in **Table 2**.

See also: **II / Extraction:** Analytical Extractions; Analytical Inorganic Extractions.

Further Reading

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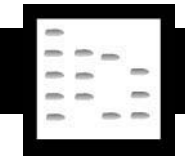
TRIGLYCERIDES



Liquid Chromatography

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Synopsis

High performance liquid chromatography (HPLC) has become a useful tool for the analysis of triglycerides from all sources. This article reviews developments for the analysis of molecular species of triglycerides, including stationary phases, mobile phases, sample solvents, detection and identification. It also points out the advantages of silver-ion HPLC and emphasizes the need for stereospecific analysis in the complete determination of triglyceride molecular species because currently this is not possible by reversed-phase HPLC. Finally, the application of HPLC to triglycerides from fats and oils is described.

Introduction

The goal of chromatographic analyses of lipids is the resolution of all classes and molecular species for the purpose of a complete identification and characterization of all the components of a fat or an oil. This characterization is not complete without the determination of their triglyceride (TG) molecular species profile. Once the fatty acid composition of a determined fat or oil is clear, the knowledge of how these fatty acids are distributed within the glycerol molecule is of major interest.

Fractionation of TGs has been carried out by different chromatographic techniques. Argentation thin-layer chromatography (Ag-TLC) has been employed to separate TG fractions, with subsequent analysis of their fatty acid methyl esters. Direct gas chromatography, using fused-silica capillary columns coated with high-temperature polar stationary phases has also been used for this purpose with rather poor results.

The introduction of chemically bonded phases and high performance liquid chromatography (HPLC) increased the usefulness of liquid chromatography for the separation of TGs. The first paper dealing with the HPLC of triacylglycerols (TGs) was published in 1975 by Pei *et al*. Simple TGs of medium-chain length were separated on a reversed-phase column. Other workers then began to use HPLC for the analysis of long-chain TGs, on silicic acid columns, reversed-phase columns, or both. The first fractionation of natural TGs by HPLC on reversed-phase columns was performed independently in 1977 by Plattner *et al*. and Wada *et al*. The later authors were the first to establish a parameter, termed the partition number (PN; PN = CN − 2ND, where CN is the total number of carbons and ND is the number of double bonds in the fatty acids constituting the TG molecule) for